

A COMPARATIVE STUDY OF THE TRACE ELEMENT GEOCHEMISTRY IN COALS FROM ALBERTA, CANADA

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INTRODUCTION

Alberta contains vast reserves (approximately 2185 megatonnes) of subbituminous and high-volatile bituminous coals, with an additional 1345 Mt considered as "indicated" and 3890 Mt as "inferred" (Smith, 1989). Virtually all of Canada's subbituminous coal resources, which are suitable for mine-mouth power generation, are found in the Interior Plains of Alberta. In addition, low sulphur ($< 1.0\%$), high-volatile bituminous, exportable thermal coals occur in the Outer Foothills region of the province. Almost 90% of Alberta's power originates from six coal-fired generating stations. These are: (1) the 1987 MW Sundance station; (2) the 766 MW Keephills station; (3) the 570 MW Wabamun Lake station; (4) the 400 MW Genesee station; (5) the 735 MW Battle River station; and (6) the 760 MW Sheerness station (Figure 1a). The first four stations are located approximately 70-100 kms to the west and southwest of Edmonton, the fifth 180 kms east of Edmonton and the sixth 160 kms northeast of Calgary.

Coal contains almost every element in the periodic table and many of the elements are released, on particles or in vapour phase, to the environment, during coal combustion. In 1991, the Alberta Research Council, along with the Geological Survey of Canada, initiated a major program, financed by the power utility companies and the Alberta Government, on the "impact of coal quality on the utilization potential of Alberta subbituminous coals". Before examining the mobilization of elements during coal combustion and their emissions to the atmosphere, it is very important to study the concentration, mode of occurrence, lateral, and vertical variation of elements in the coal seams currently mined or those to be mined, within the boundaries of the minesite. As a result, this study deals with the elemental concentration and variation in coals from the Highvale mine (feedstock for the Sundance and Keephills plants), Whitewood mine (Wabamun plant), Vesta mine (Battle River plant) and Obed Mountain coal deposit (exported to Ontario as thermal coal) (Figure 1b).

The main focus of the paper is on the concentration of selected trace elements with known toxic responses to humans and the biological system, when emitted by coal-fired power stations, such as As, Hg, Mn, Se, and V, to name but a few. The elements in coals from the above mines will be classified according to the mode of their occurrence, with particular emphasis on the geological and geochemical factors influencing their distribution in the coal-bearing succession. Elemental concentrations will be compared and contrasted on a mine-by-mine basis rather than a seam-by-seam basis.

RESULTS AND DISCUSSION

Highvale Mine

Some of the elements of great concern because of their environmental effects are mercury (Hg) and cadmium (Cd). Mercury is volatile and is found either in gaseous form or enriched on the surfaces of fine particles following coal combustion (Clarke and Sloss, 1992). It is readily available for plant uptake and could be responsible for neural, renal and cardiovascular diseases in humans (US DOE, 1989). The Highvale coals contain Hg in the 100 to 400 ppb range (Gentzis, 1993, unpublished data), values which are slightly higher than Australian coals (100 ppb; Swaine, 1990) and lower than US coals (180 ppb; Finkelman, 1980). Low-sulphur coals, such as the Highvale coals (total S $< 0.5\%$), are generally low in Hg and the element is believed to have an inorganic association. Cadmium tends to bioaccumulate in the food chain (Neme, 1991) and is a possible carcinogen to humans and animals (US DOE, 1989). The Highvale coals have Cd content less than 0.2 ppm, values similar to Australian coals (0.01-0.02 ppm) (Swaine, 1990) and lower than US coals (1.3 ppm) (Finkelman, 1980).

Mean elemental concentrations in the Highvale coals are: As (3.82 ppm), Br (286.4 ppm), Cl (72.3 ppm), Cr (11.5 ppm), Cu (20.6 ppm), Se (1.65 ppm), U (2.57 ppm), Th (5.6 ppm), and V (17.1 ppm) (Gentzis *et al.*, 1993). The high concentration of Br in some coal samples is attributed to drilling mud contamination, a phenomenon also observed by Finkelman (*pers. commun.*, 1993) in coals from Pakistan. Sodium content averages 2500 ppm, approximately three times higher than the nearby (12 kms) Whitewood mine coals. This element has an inorganic association in the Highvale coals, and any detrimental effect of Na may be compensated by Ca in the coals. Other elements with an inorganic association include As, Ba, Cs, Fe, K, Mg, Mo, U, and V; Sr and Ce show an intermediate association, while Br, Cl, B, Co, Dy, and Mn show an organic association. The elements Al, As, Sc, Th and all rare earth elements (REEs) tend to decrease from roof to floor of the coal seams and their concentration often shows a cyclical pattern within the coal-bearing strata, indicative of periods of inundation of the coal-forming environment by clastic sediments.

Crowley *et al.*, (1989) have explained a mobilization pattern when a volcanoclastic layer (tonstein) is located above coal beds using cluster analysis. According to Van der Flier-Keller (1993), the light rare earth elements (LREEs) are associated with clay minerals and the heavy rare earth elements (HREEs) with detrital heavy minerals. All REEs in the Highvale mine subbituminous coal closely follow the Al trend, a behaviour which is expected since the REEs are associated with the inorganic constituents in coals. The high concentration of REEs in the thin coal seam 3 in drillhole HV84-901, which is located underneath a Sr and Ba-rich tonstein band (Figure 2), is believed to be due to migration of the elements by groundwater and subsequent concentration in the coal. The coal seam contains more HREEs than the volcanoclastic layer above because the HREEs were preferentially hydrolyzed or bound to organic complexes and allowed to migrate from the tonstein. The LREEs, being mobile, when liberated during the breakdown of the parent volcanic ash caused by weathering, were preferentially accommodated in clay minerals. The REE pattern in the Highvale coal is thought to be controlled by source lithology (volcanic versus sedimentary partings), by weathering, and other geochemical patterns during and after coal formation.

Ashing of two suites of samples of Highvale coal at 120°C resulted in an enrichment of all elements by a factor of x1.5 to x6.5 in one suite and by x5 to x11 in the other. In the 400°C ashed sample, enrichment factors ranged from x1.5 to x6.5 in the first suite and by x1.5 to 9.5 in the second. The elements Br, Cl, and Se were, surprisingly, enriched by x2 to x6, pointing to the formation of salts (i.e. bromide salts), which occurs as a result of reactions of anions with cations during ashing. At 800°C, Br and Cl were completely volatilized, as expected. Relative enrichment factors (REF), calculated using two methods of the ratio of elemental concentration versus Al concentration in air/crust (method A) and in ash/coal (method B) show method B to give higher and more consistent values.

Generally, there is little information on the variation of elements in coal seams laterally over a long distance, mainly due to variations in basement conditions and other geological factors (folding and faulting). The concept of "variance ratio" (the ratio of maximum to minimum value of an element) was first introduced by Headlee and Hunter in 1953 and subsequently used by Zubovic (1960) and Swaine *et al.*, (1984). The lateral variation of selected elements in pits 3 and 5 of the mine for seams 1 and 2 (the thickest) and corresponding variance ratios show that elements with inorganic association in the Highvale coal (ie. As, Na, U, Se and Th) have narrow lateral variations in the pits and low variance ratios, whereas elements with organic association (ie. Br, Cl) have wider lateral variation and higher variance ratio.

Whitewood Mine

The following seams are present in this mine: 1U, 1L, 2, 3, 4, 5, and 6, of which seam 1U is not presently mined and seam 1L is stratigraphically correlatable to seam 1 in the nearby Highvale mine. The mean concentrations of elements are: As (4.7 ppm), Br (15.1 ppm), Cl (21.5 ppm), Co (3.3 ppm), Cr (7.0 ppm), Mo (4.8 ppm), Na (710 ppm), Mn (110 ppm), U (2.5 ppm), Th (6.0 ppm), and V (19.3 ppm) (Gentzis, 1993, unpublished data). Compared to the Highvale coals, these coals are slightly enriched in As and V, depleted in the halides Br and Cl, also in Ba, Cr, Na, Se, and have similar concentration of Co, Mn and U. By world standards (see Clarke and Sloss, 1992, Table 8, p. 26), the Whitewood mine coals are "clean" and suitable for utilization. The ash analysis shows the mean SiO₂ value for all seams to be between 50 and 70 wt.%, Al₂O₃ ranges from 12-27 wt.%, Fe₂O₃ ranges from 1.5-6 wt.%, TiO₂ ranges from 0.4-0.75 wt.%, and CaO is in the 6-15 wt.% range. In addition, MgO varies from 0.6-2.1 wt.%, K₂O from 0.15-0.55 wt.%, Na₂O from 0.4-0.8 wt.% (except for seams 3 and 6) and

SO₃ from 2-6 wt.% (TransAlta Utilities, 1993, unpublished data). The coal ash is depleted in Na₂O and enriched in SO₃ and CaO (lime) compared to the coal ash quality requirements for power generation, outlined by Skorupska (1993). The ash content of the coal is 12-25%, with the exception of seam 1U (37%). A coal containing 20% ash provides an uncontrolled dust loading of 30 g/m², therefore, a collection efficiency of 99.7% is required to meet acceptable emission standards (Skorupska, 1993). In the Wabamun Lake power station, electrostatic precipitators (ESPs) are used to achieve this objective. One problem related to ESP performance in the Wabamun plant is opacity, which results in a decrease in precipitator efficiency. Because the Na₂O content in the ash is lower than the standard requirements dictate, the fly ash resistivity increases resulting in a decrease of the corona current flow.

Vesta Mine

One of the most obvious differences in trace elements between coal from this mine and coal from the other three mines is its high boron (B) content (> 200 ppm) (Gentzis, 1993, unpublished data). Boron in coal is interesting from a geochemical point of view because it can differentiate whether freshwater, mildly brackish, or brackish water conditions prevailed during the early stages of coal formation (Swaine, 1971; Goodarzi and Van der Flier-Keller, 1989; Banerjee and Goodarzi, 1990). Boron is very sensitive to changes in water salinity and remains constant laterally within a minesite. Furthermore, B values usually fall nicely within the limits designated for each generalized depositional setting (< 50 ppm for freshwater, 50-110 ppm for mildly brackish and >110 ppm for brackish) unless there is a secondary B enrichment (Goodarzi and Swaine, 1992). The B content of the Vesta mine coal indicates that the peat interacted with brackish waters, which may have invaded the fluvio-deltaic depositional setting during a marine transgression. Boron in the Vesta mine coal is associated with the organic matter and is depleted (25 ppm) only in one, inertinite-rich sample. The petrological composition of the sample indicates exposure of the peat surface to fire or oxidation and higher temperatures. Depletion of B has been observed in oxidation and combustion zones of naturally heat-affected coal seams (Goodarzi and Swaine, 1993) and is attributed to possible volatilization of the element. During combustion of this coal, B will most likely be redistributed in the bottom ash, the flyash retained by ESPs and fine flyash, which will eventually reach the atmosphere with the stack gases. However, B is not considered to be toxic and may have little detrimental effect in the close environs of the Battle River power station. The Vesta coals are very low in As (<1.0 ppm), Br (<2.3 ppm), V (<3 ppm), U (<1.4 ppm), Mn (<30 ppm), Mo (<2.5 ppm), but are extremely high in Na (range is 4200-4900 ppm) (Gentzis, 1993, unpublished data).

Obed Mountain Mine

The B content of the coal ranges from 27 to 100 ppm, but generally it is < 50 ppm, indicating freshwater to possibly slightly brackish water depositional environment. The element is depleted in the sedimentary partings (12-27 ppm) and enriched in the coal intervals immediately underneath. This behaviour points to downward mobilization of B from parting to coal of soluble to groundwater B, a phenomenon believed to be enhanced by increased oxidation leading to formation of leachates containing enough soluble B to affect groundwater (Goodarzi and Swaine, 1993). The range in elemental concentration in the two thickest seams are as follows: As 2-7.6 ppm; Br 5.9-10.1 ppm; Cl 76.4-87.2 ppm; Cr 3.4-11.2 ppm; Co 1.2-2.9 ppm; Mn 21.5-39.3 ppm; Mo 2.1-5.5 ppm; Se 1-1.2 ppm; U 1-2 ppm; Th 1.2-2.8 ppm (Gentzis, 1993, unpublished data); the lack of Na (mean is 117 ppm) could lead to potential problems in ESP performance.

Most elements increase in concentration with ash content, thus are inorganically associated in the coal. The vertical variation of certain elements is very similar, such as Th and U; also Zn, Rb, Cs, and K; Br and Cl; Na, Mg, Ti, As, and Fe. It was observed that U, Se, Sb, and Mo were concentrated preferentially in the upper part of the seams, while Br and Cl were enriched in the middle part. The elemental pairs: Mn and Sc, Co and Cu, Se and U, Rb and Cs, and the HREE are concentrated in coal intervals immediately underneath roof sediments or major partings. The Obed Mountain coals are depleted in most elements compared to coals formed under freshwater conditions, such as Highvale and Whitewood, except for Cl.

CONCLUSION

The elemental concentrations in the subbituminous coals from Alberta are related to the environment of coal deposition, the presence of volcanoclastic layers (tonsteins), the action of groundwater, the degree of weathering, and the nature of country rocks. The coal seams studied contain low concentrations of environmentally or industrially-sensitive elements, such as As, B (except for the Vesta coal), Cl, Mo, Se, Na, Ca, U,

and S, both vertically and laterally. The coals are "clean" and suitable for utilization. Elements associated with the mineral matter in coal are concentrated in the 800°C ashed coal, when compared to the fresh coal. There is also a progressive concentration of Br from the fresh to the 120°C and the 400°C ashed samples, pointing to the formation of salts.

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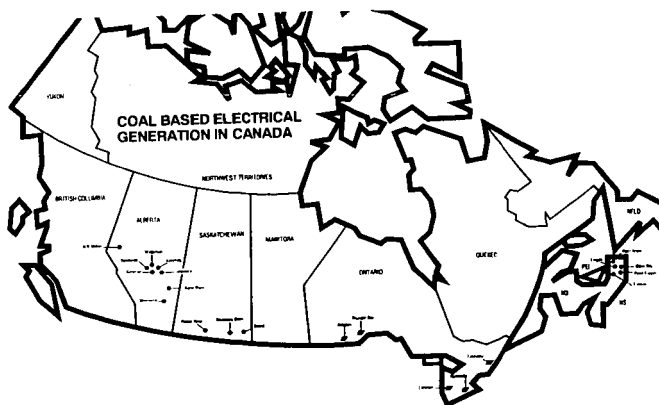


Figure 1a. Map of Canada showing location of power stations in Alberta (after Canadian Coal Association Directory, 1993).

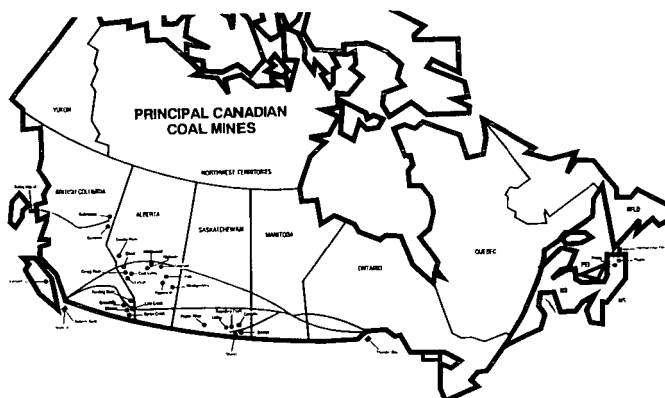


Figure 1b. Map of Canada showing location of coal mines in Alberta (after Canadian Coal Association Directory, 1993).

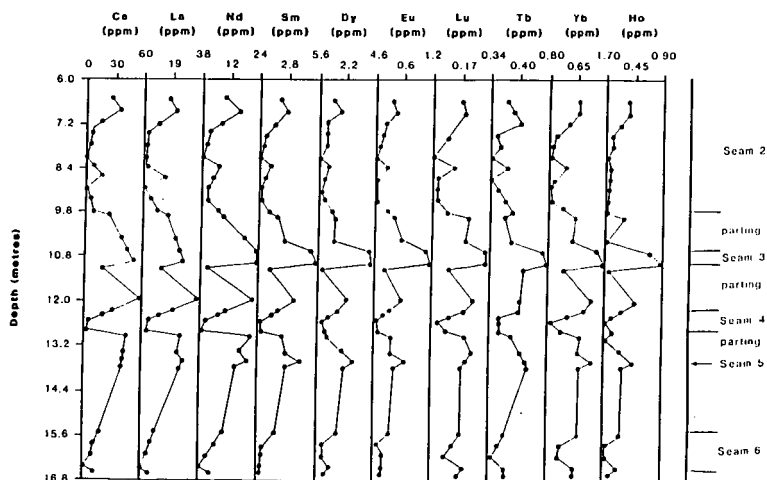


Figure 2 Vertical variation of REEs in drillhole HV84-901, Highvale mine.